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U. S. Department of the Interior
Bureau of Mines
Spokane Research Center
East 315 Montgomery Avenue
Spokane, WA 99207

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	min	minute
g	gram	mL	milliliter
g/L	gram per liter	pct	percent
h	hour	vol pct	volume percent
L	liter		

PREPARATION OF AMMONIUM PARATUNGSTATE FROM A SODIUM TUNGSTATE-SODIUM CHLORIDE PHASE

By A. E. Raddatz,[1] J. M. Gomes,[2] and T. G. Carnahan[3]

ABSTRACT

Previous Bureau of Mines research has shown that tungsten ores containing as little as 40 pct WO_3^{2-} can be processed by a high-temperature molten-salt extraction technique to produce a tungstate-bearing sodium chloride phase with 99 pct W recovery and little impurity contamination. The objective of this work was to demonstrate that the tungstate-bearing sodium chloride phase can be a suitable feed material for preparing ammonium paratungstate (APT) by a modification to the present industrial solvent extraction process. A combined crossflow-countercurrent flow solvent extraction technique to extract tungsten is presented. APT produced by this new technique contained 88.6 pct WO_3^{2-} and the following impurities, in percent: MnO_2 0.0007, MoO_2 0.017, P_2O_5 <0.010, and SiO_2 0.012. Implementation of this processing technique would improve tungsten recovery from concentrates and simplify processing operations.

[1]Supervisory chemical engineer.
[2]Supervisory metallurgist (retired).
[3]Supervisory physical scientist.
Reno Research Center, Bureau of Mines, Reno, NV.

INTRODUCTION

APT, $5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$, is the first intermediate product in the preparation of tungsten metal or tungsten carbide. More than 75 pct of all tungsten consumed in the United States is first processed to APT. Figure 1 shows how APT is prepared by alkali pressure digestion of scheelite or wolframite concentrates to yield a sodium tungstate solution. The solution is purified to remove harmful impurities such as molybdenum, phosphorus, arsenic, and silica. The purified solution is treated by a solvent extraction process (liquid ion exchange) to recover a crystalline APT product.

One of the problems with the conventional solvent extraction process is possible pollution of the environment from alkaline effluents and discharged residues. A second problem arises when radioactive minerals contained in some wolframite ores generate residues requiring special handling and storage permits. A third problem is the time, cost, and tungsten losses in purifying the pregnant solution to make it an acceptable feed for the solvent extraction step. Silica, molybdenum, arsenic, and phosphorus are removed in separate precipitation and filtration operations which incur a 2- to 3-pct loss of tungsten.

A high-temperature molten-salt extraction technique previously developed by the Bureau of Mines offered a new approach for preparing APT from scheelite and wolframite concentrates that could overcome these problems.[4] Ore decomposition and most of the purification are accomplished in one step by this technique. Wolframite or scheelite is decomposed in a two-phase sodium chloride-sodium metasilicate melt at 1,050° C. The sodium chloride and sodium metasilicate phases are immiscible at this temperature and allow metals separation to be achieved because tungsten is concentrated in the halide phase, while iron, manganese, and calcium report to the silicate phase. The two molten phases are separated by decantation. The molten silicate phase is quenched in water to recover the small amount of water-soluble sodium tungstate that would be lost with the silicate phase. The tungstate-bearing halide phase is readily soluble in water, and tungsten is recoverable from the resulting pregnant and quench solutions by the conventional solvent extraction technique described above. Figure 2 shows a flow sheet for the proposed process sequence.

Substitution of the Bureau's high-temperature molten-salt extraction process for the alkali digestion and solution purification steps in the conventional process would eliminate the pollution problems and save processing time. Another potential benefit is that the residue from the molten-salt extraction process step is a refractory silicate slag that contains strategic commodities such as columbium, scandium, and tin. Since this residue is insoluble in water and resists weathering, it could be stored without degradation and processed later for recovery of its contained metallic values. A cursory study of possible techniques to recover these commodities is presented in the appendix.

[4]Gomes, J. M., K. Uchida, and D. H. Baker, Jr. A High-Temperature, Two-Phase Extraction Technique for Tungsten Minerals. BuMines RI 7106, 1968, 13 pp.

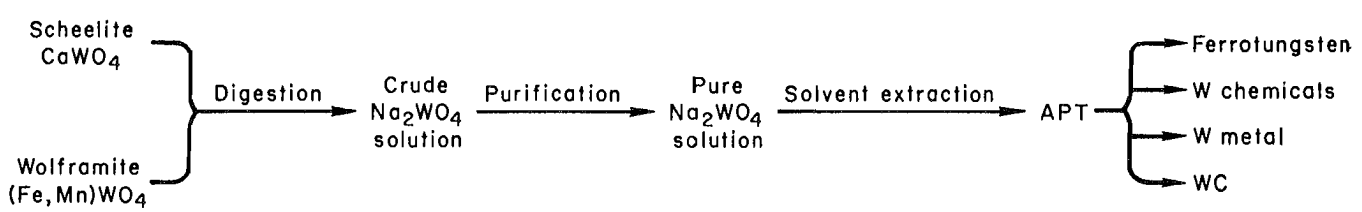

FIGURE 1.—Tungsten production from scheelite and wolframite concentrates.

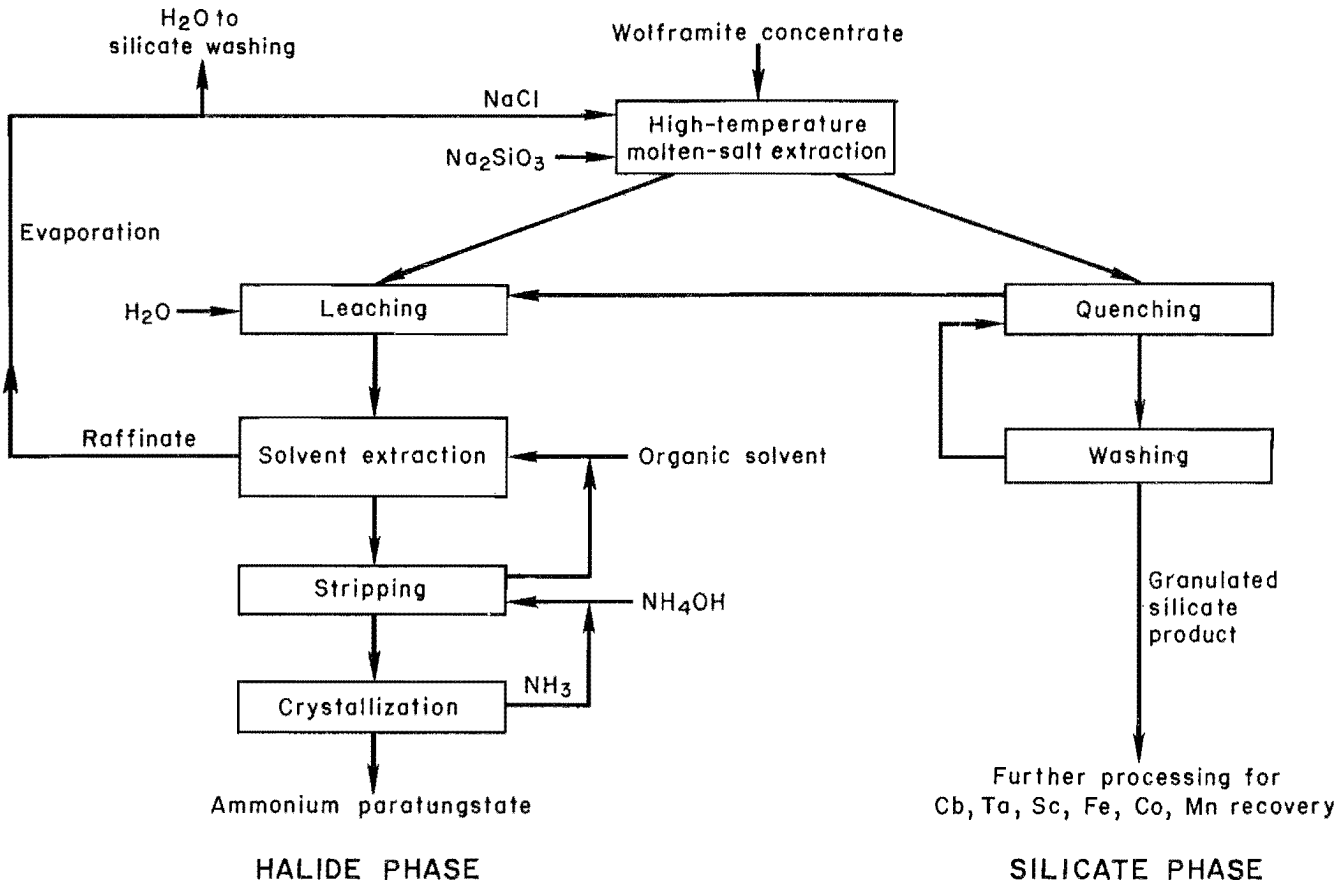

FIGURE 2.—Proposed flowsheet for solvent extraction process to recover APT from wolframite via high-temperature molten-salt extraction.

The objective of this investigation was to show the feasibility of using the tungstate-bearing halide phase prepared from a domestic wolframite ore as a feed material for the commercial solvent extraction process and to determine if quality APT can be prepared from this material with less purification of the pregnant solution. A combined crossflow-countercurrent flow solvent extraction circuit was devised to extract tungsten efficiently from the sodium chloride-bearing solutions.

ACKNOWLEDGMENT

The authors thank L. E. Schultze, supervisory chemist, Reno Research Center, Bureau of Mines, Reno, NV, for discussions that led to the design of the combined crossflow-countercurrent flow solvent extraction unit.

MATERIALS AND EXPERIMENTAL PROCEDURE

A wolframite concentrate was decomposed by the high-temperature molten-salt extraction technique to produce samples of the halide phase, which were dissolved to prepare solutions for the solvent extraction process step. Analysis of the wolframite concentrate showed that iron and manganese were the only major impurities (table 1).

Because limited quantities of actual halide leaching solution would be available due to the small amount of the halide phase, initial solvent extraction experiments were conducted with synthetic tungstate-bearing halide solutions to determine the effect of pH on tungsten extraction. This research was conducted

TABLE 1. - Analysis of wolframite concentrate, percent

Constituent		Constituent	
WO_3^{2-}.....	67	MgO.....	0.04
Al_2O_3.....	.5	MnO_2.....	16.6
As_2O_3.....	<.004	MoO_2.....	.03
CaO.....	<.01	Na_2O.....	.014
Cb_2O_5.....	1.22	P_2O_5.....	.08
Fe_2O_3.....	10.1	SiO_2.....	1.0
K_2O.....	<.05	TiO_2.....	.4

before the composition of the actual halide phase leach solution was established and its composition was considerably different from the synthetic solution's composition. The equilibrium diagram used for designing the solvent extraction system was generated from actual leaching solution. Solutions were prepared by dissolving sodium tungstate and sodium chloride in water. Technical-grade anhydrous Na_2WO_4 and food-grade sodium chloride were used. Analyses of the solution gave the following concentrations, in grams per liter: WO_3^{2-}, 32; Na_2O, 34; and NaCl, 48.

Actual halide phase leaching solutions used for the solvent extraction study were prepared by dissolving the halide phase with the aqueous solution used to quench the silicate phase. A total of 1,070 g of halide phase was dissolved in 3 L of quench solution at room temperature in 3 h. The resultant halide solution was diluted to twice its volume to optimize tungsten loading of the organic phase. Exploratory tests showed that the presence of NaCl would depress loading of tungsten. For example, Primene JM-T[5] solvent could be loaded to 55 g WO_3^{2-} per liter from a solution containing 62 g WO_3^{2-} per liter in the absence of NaCl, but its loading was limited to 28 g WO_3^{2-} per liter in the presence of 153 g NaCl per liter. High concentrations of sodium chloride also caused formation of a tungsten-laden third phase that interfered with phase separation and

[5]Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 2. - Composition of diluted pregnant quench-leaching solution for solvent extraction, grams per liter[1]

Constituent		Constituent	
WO_3^{2-}.....	42	MgO.....	<0.010
NaCl.....	105	MnO_2.....	.002
Al_2O_3.....	<.030	MoO_2.....	.002
As_2O_3.....	<.020	P_2O_5.....	<.050
CaO.....	<.030	SiO_2.....	<.020
Fe_2O_3.....	<.001	TiO_2.....	<.002
K_2O.....	.260		

[1]Reported as grams of oxide per liter to be consistent with current industrial practice.

increased tungsten losses. Increasing the solvent extraction temperature to 55° C did not decrease emulsion formation or increase tungsten extractions. Analysis of the halide solution showed that iron and manganese were removed in the high-temperature solvent extraction step (table 2).

Primene JM-T was chosen as the organic extractant on the basis of Bureau research and industrial practice, which indicated that tungsten could be extracted from alkali solutions with primary amines.[6] Composition of the organic solvent was 5 vol pct Primene JM-T diluted in 85 vol pct kerosene with 10 vol-pct decanol as a phase modifier.

Solvent extraction experiments were conducted with 1,000-mL separatory funnels at room temperature. Prior to extraction, the pH of each halide solution was adjusted to 2 or 4 with sulfuric acid and continually monitored while the adjustment was made. The organic solvent was conditioned by washing with an equal volume of 1M H_2SO_4. The wash was discarded. The conditioned solvent was

[6]Churchward, P. E., and D. W. Bridges. Tungsten Recovery From Low-Grade Concentrates by Amine Solvent Extraction. BuMines RI 6845, 1966, 17 pp.

Yih, S. W. H., and C. T. Wang. Tungsten Sources, Metallurgy, Properties, and Applications. Plenum Press (NY), 1979, pp. 79-128.

gently shaken in a separatory funnel with the acidified halide solution for 15 min to ensure phase equilibration. After phase separation, the raffinate was sampled, and the loaded solvent was washed with an equal volume of water to remove traces of entrained raffinate and sampled. Tungsten was stripped from the loaded solvent by gentle agitation for 10 min with an equal volume of 3N NH_4OH. The loaded strip solution was evaporated by boiling to decrease its volume by one-half and held at room temperature for at least 12 h to crystallize APT. APT crystals were recovered by filtration and washed with water to remove traces of the NH_4OH strip solution. The quantity of wash water was kept minimal because APT is water soluble. The volume of wash solution was measured and samples were taken to determine tungsten recovery.

Solutions and solids were analyzed by X-ray fluorescence for tungsten. Other elements were determined by atomic absorption spectroscopy, inductively coupled plasma spectroscopy, and emission spectroscopy.

RESULTS AND DISCUSSION

Preliminary experiments using the synthetic halide solution were conducted to determine appropriate experimental conditions for solvent extraction. Timed extraction tests were conducted to determine the effect of contact time on the extent of extraction at pH values of 2 and 4. Contact time was varied from 1 to 20 min. The results are shown in figure 3. Two minutes were required to equilibrate the system. Almost identical characteristics were measured at pH 2 and 4. While differences were small, extraction after 2 min contact time was slightly better at pH 2 (98 pct) than at pH 4 (92 pct). Figure 4 shows results of solvent extraction when applied to the actual halide solution. At pH 4, extraction was lower than at pH 2. During the first 2.5 min of contact time, 87 and 75 pct of the tungsten was extracted at pH 2 and 4, respectively; with extraction slowly increasing with time. Residual tungsten concentration in the raffinate was higher and the contact time slightly longer for the actual solution than for the synthetic solution. These differences were due to higher sodium chloride concentrations in the actual halide solution. Phase separation was much better at pH 4 than at pH 2.

The remaining solvent extraction experiments were conducted with the actual halide solution at pH 4 because of better phase separation. Contact time was set at 15 min to ensure near equilibrium conditions. Phase ratios (volume of organic phase to volume of aqueous phase) investigated were 1:10, 1:7.5, 1:5, 1:1, 5:1, 7.5:1, and 10:1.

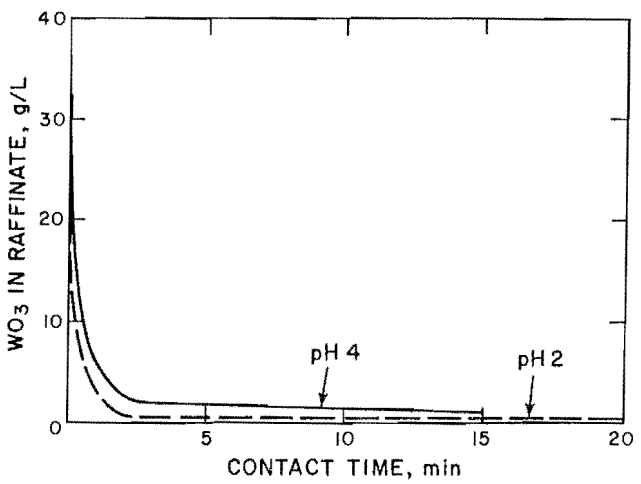

FIGURE 3.—Tunsten extraction from synthetic solution as a function of time.

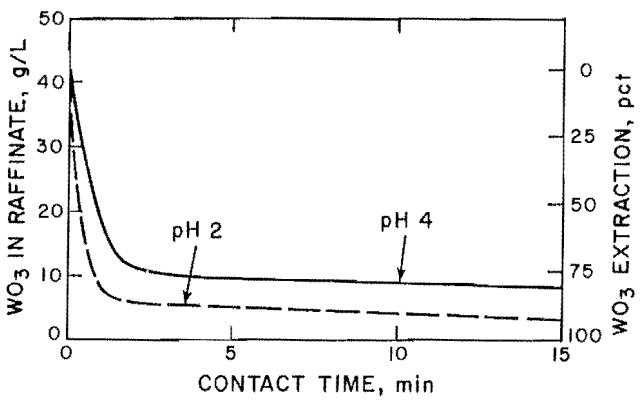

FIGURE 4.—Tungsten extraction from actual halide solution as a function of time.

TABLE 3. - Tungsten balance, percent

O-A ratio, vol pct.....	1:10	1:7.5	1:5	1:1	5:1	7.5:1	10:1
Raffinate.....	89	85	79	21	0.2	0.1	0.4
Loaded organic wash....	.02	.02	.03	.2	1	1.5	2
Depleted strip solution	3	4	9	25	17	22	15
APT.....	7	9	11.5	47	74	69	71
Losses.....	1	2	.5	7	8	7.5	11.5

An equilibrium curve was determined in a set of single-contact tests (fig. 5). The curve is characterized by a steep slope up to organic phase loading of 30 g WO_3^{2-} per liter or more and then becomes flat, which indicates favorable solvent extraction loading similar to nonchloride tungstate solutions.[7]

During development of the equilibrium curve, stable emulsions were observed when organic-to-aqueous phase ratios were greater than 1. This poor phase separation manifested itself in excessive tungsten losses (table 3). Tungsten losses ranged from 0.5 to 11.5 pct and were acceptably small (2 pct or less) only at phase ratios of 0.2 or less. Crud formation accounts for a majority of the tungsten losses. Emulsions could be avoided by using a phase ratio less than 1, but tungsten extraction would be incomplete. This required a modification of the normal multiple-contact countercurrent solvent extraction flow diagram.

A novel solvent extraction system was devised to extract the tungsten efficiently at phase ratios less than 1 (fig. 6). The solvent stream was divided into three multiple streams, two of which needed only to contact the tungstate solution once to be fully loaded. The third stream was employed in the normal countercurrent manner. Calculations (fig. 5) indicated that for a feed solution of 42 g WO_3^{2-} per liter and phase ratio of 0.5, the aqueous WO_3^{2-} concentration would be decreased to approximately 10 g/L after the second stage of the crossflow portion of the circuit. This WO_3^{2-} concentration is now low enough to allow the use of a McCabe-Thiele diagram (fig. 5) to determine the number of stages needed in the normal countercurrent flow solvent extraction train. Using an operating line with a slope of 2 and a feed concentration of 10 g WO_3^{2-} per liter, figure 5 shows that two stages of countercurrent flow solvent extraction would be needed to decrease the WO_3^{2-} concentration in the raffinate to less than 1 g/L. Bench-scale simulation of two stages of crossflow solvent extraction followed by two stages of conventional countercurrent solvent extraction was conducted in batch, separatory-funnel equilibrium shake-out tests. Two cycles were required for solutions to reach constant compositions. Experimental results (table 4) indicate that the predictions were correct.

[7]First work cited in footnote 6.

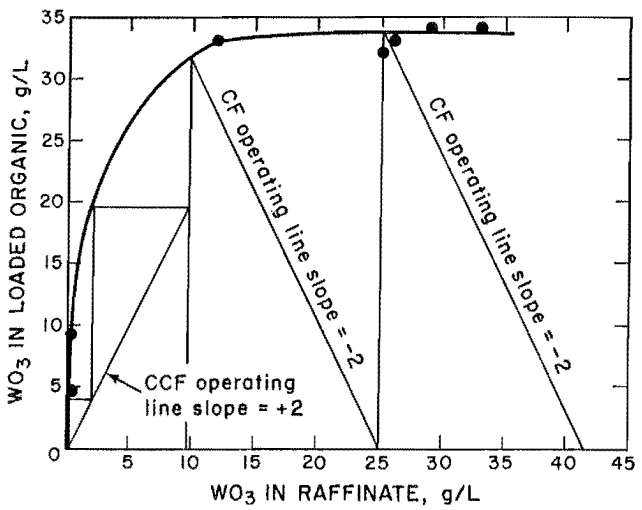

FIGURE 5.—Equilibrium diagram for extraction of tungsten with Primene JM-T using a two-stage countercurrent flow (CCF) solvent extraction circuit.

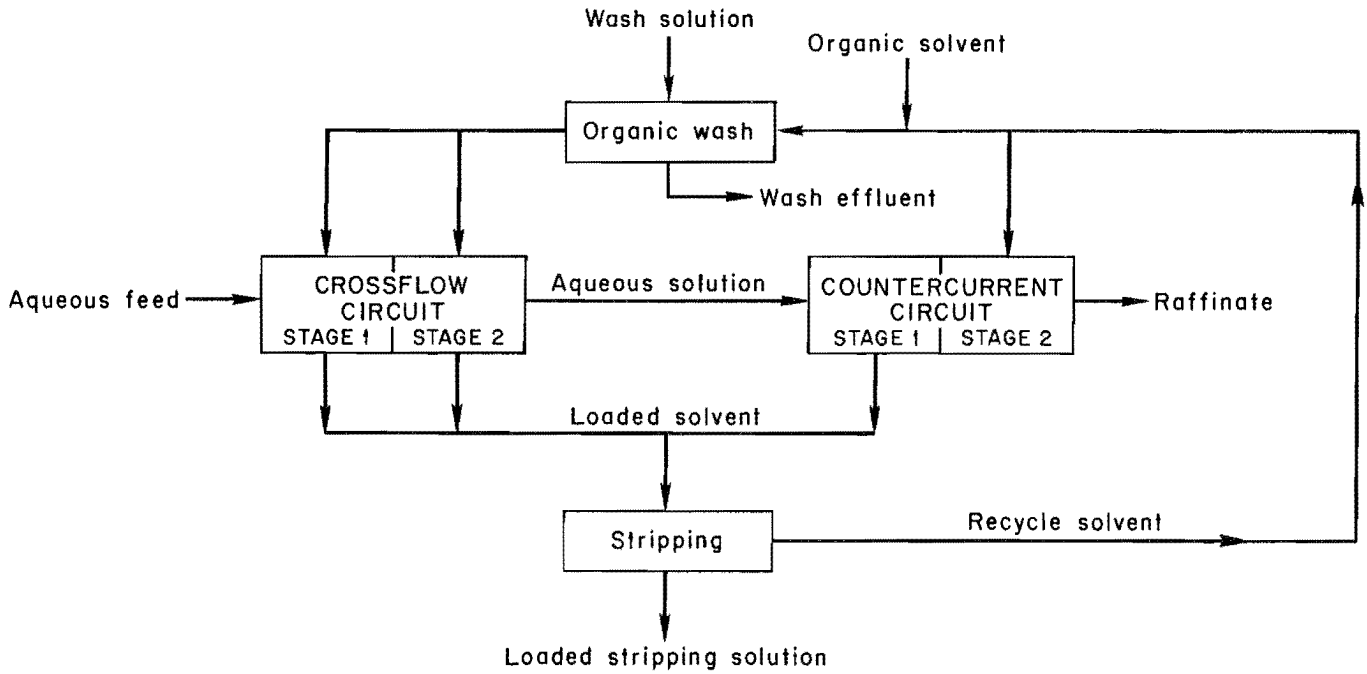

FIGURE 6.—Combined crossflow-countercurrent flow solvent extraction circuit for maintaining overall phase ratio at less than 1.

TABLE 4. - Tungsten extraction to the organic phase in combined crossflow-countercurrent flow solvent extraction system at phase ratio of 0.5, percent

Stage	Extraction
Crossflow:	
Stage 1	37
Stage 2	40
Countercurrent flow:	
Stage 1	20
Stage 2	2
Total	99

TABLE 5. - Analyses of Bureau of Mines and commercial APT, percent

	Bureau	Commercial
WO_3^{2-}	88.6	88.3
As_2O_3	<.004	<.004
CaO	<.005	<.005
Fe_2O_3	<.0004	<.0004
K_2O	<.02	<.02
MnO_2	.0007	<.00005
MoO_2	.017	<.0005
Na_2O	<.005	<.005
P_2O_5	<.010	<.010
SiO_2	.012	.009
TiO_2	<.0005	<.0005

The stripped organic solvent contained less than 0.01 g WO_3^{2-} per liter. After crystallization of APT from the ammonium tungstate solution, the APT product was analyzed for WO_3^{2-} content and impurities. A typical product contained 88.6 pct WO_3^{2-}. Stoichiometric WO_3^{2-} content of the pentahydrate form of APT is 88.1 pct. X-ray diffraction identified the product as $5(NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$ with a possible trace of $5(NH_4)_2O \cdot 12WO_3 \cdot 11H_2O$.

A comparison of the APT product purity with a commercial APT produced from scheelite is given in table 5. The Bureau product was only slightly higher in manganese, molybdenum, and silica. The extremely low manganese value in the commercial APT is because its feed,

scheelite, has little manganese, whereas the wolframite used by the Bureau contained 16.6 pct MnO_2. Of the most troublesome impurities--molybdenum, phosphorus, silica, and sodium--only molybdenum and sodium could present problems because they are coextracted with tungsten during solvent extraction. If molybdenum concentrations reach problem levels, the aqueous feed solution can be treated by sulfide precipitation methods currently used in the industry to decrease molybdenum contamination.[8] Sodium can be eliminated by washing the loaded organic solvent with a dilute 5-g/L ammonium sulfate solution.[9]

CONCLUSIONS

Previous studies showed that tungsten minerals are decomposed at 1,050° C in a sodium chloride-sodium silicate melt and yield two immiscible phases, a tungstate-bearing sodium chloride phase and a silicate phase. This investigation demonstrated that the tungstate-bearing sodium chloride phase can be utilized as feed for preparing APT by the conventional solvent extraction process. The halide phase, containing 99 pct of the tungsten, can be dissolved in the solution from quenching the silicate phase to produce a tungstate solution. Tungsten can be recovered by solvent extraction with a primary amine extractant, stripped with an ammonium hydroxide solution, and crystallized as APT from the strip solution. The Bureau's APT product contained 88.6 pct WO_3^{2-}.

[8]Second work cited in footnote 6.

[9]Hughes, M. A., and C. Hanson. The Fate of Impurities in a Liquid-Liquid Extraction Process for Tungsten. Pres. at 112th AIME Annu. Meet., Atlanta, GA, Mar. 6-10, 1983, 11 pp.; available from M. A. Hughes, Sch. of Chem. Eng., Univ. of Bradford, Bradford, West Yorkshire, UK.

APPENDIX

The silicate phase from the high-temperature molten-salt extraction process represents a potential source of strategic commodities such as columbium, scandium, and tin (table A-1). Another resource in the tungsten industry is wolframite processing residues. A cursory investigation into possible techniques to recover these commodities from each feed was conducted with the following results.

Silicate Phase

The molten-salt extraction technique for the decomposition of tungsten ores separates tungsten from iron, manganese, columbium, and other minor constituents found in the ore. More than 90 pct of the components other than tungsten are concentrated and recovered in the silicate phase. Analyses of silicate phases obtained by treating these wolframite concentrates are shown in table A-1.

TABLE A-1. - Analyses of silicate phases of wolframite concentrates treated by the high-temperature molten-salt extraction technique, percent

Constituent	1	2	3
WO_3^{2-}	0.8	0.4	0.7
Al_2O_3	.4	1.7	1.2
CaO	1.0	7.1	.7
Cb_2O_5	.9	.3	.9
Fe_2O_3	13.6	15.3	12.2
K_2O	ND	.06	.07
MgO	.5	.3	.4
MnO_2	25.3	8.6	16.2
MoO_2	<.01	.01	.02
Na_2O	18.2	17.2	20.4
P_2O_5	.01	.07	.07
SiO_2	43.7	35.9	26.6
TiO_2	1.0	.6	.9
Sc	.2	.05	ND
Sn	.3	1	.2

ND Not determined.

Mineralogical examination of the nonmagnetic portion of silicate phase 3 with a scanning electron microscope (SEM) showed--

- No distinct columbium phase was found.
- Predominant phase was a manganese-iron silicate with inclusions of manganese, iron, chromium, and titanium.
- Tungsten occurred in distinct sponge-like grains.

Since columbium was not observed in discrete grains, it was concluded that it was disseminated throughout the Mn-Fe silicate phase. Techniques were evaluated for the recovery of columbium. A summary of the reagents studied and the composite extractions obtained are presented in table A-2. No extraction occurred with NH_4Cl, $(NH_4)_2SO_4$, $KHSO_4$, KOH, and Na_2CO_3. The most successful technique involved mixing five parts silicate phase with one part sodium fluoride or potassium fluoride, roasting at 1,050° C for 2.5 h, quenching in 1.5 L of water, and leaching the quenched silicate in a 0.5-L 25-vol-pct sulfuric acid solution at 90° C for 3 h. Sixty-six percent of the columbium was extracted. The technique was not selective because iron and manganese were also solubilized. Scandium was extracted with a $FeSO_4$-H_2SO_4 lixiviant or a sodium fluoride roast and H_2SO_4 leaching technique.

TABLE A-2. - Reagents used in leaching silicate phase and extraction, percent

Technique and reagent	Cb	Fe	Mn
Roast-leaching:			
$KF-H_2SO_4$	66	88	80
$NaF-H_2SO_4$	66	90	78
Leaching:			
$FeSO_4$	0	25	2
$FeSO_4+H_2SO_4$	0	29	63
H_2SO_4	24	79	90
H_2SO_3	0	80	86

Wolframite Processing Residues

Industrial residues from processing wolframite concentrates contained columbium, tantalum, cobalt, and scandium in a high iron-manganese matrix and had the analyses shown in table A-3.

TABLE A-3. - Analyses of wolframite processing residues, percent

Constituent	1	2	3	4
WO_3^{2-}.....	3.3	2.1	5.1	2.5
Al_2O_3.....	2.0	2.0	7.0	2.0
Bi_2O_3.....	.6	<.2	<.2	<.2
CaO.....	12	5.2	5.5	2.1
Cb_2O_5.....	1.3	.5	.8	2.0
CoO.....	.3	1.3	0	0
Fe_2O_3.....	29	30	39	38
MgO.....	2.8	5.0	.3	.2
MnO_2.....	15	23	19	22
Sc.....	.03	<.01	.01	.01
SiO_2.....	13	10	11	1.6
SnO_2.....	.5	.08	.4	.9
Ta_2O_5.....	.4	.09	.2	.6
Au.....	[1].02	0	[1].05	0
Ag.....	[1]1.4	[1].6	[1].6	[1].1

[1]Ounce per ton.

Mineralogical examination of residue 1 identified wolframite, ferberite, cassiterite, scheelite, arsenopyrite, xenotime, columbite and tungsten-bearing columbite.

Techniques were investigated to treat the processing residues. A summary of the reagents evaluated and composite extractions obtained from the four residues are given in table A-4. No extractions occurred in atmospheric leaching with Na_2CO_3, Na_2CO_3+NaOH, or NaOH. A sulfuric acid roast at 950° C followed by water leaching extracted 95 pct of the manganese, 91 pct Co, and 81 pct Sc. Columbium and tin remained in the leached residue.

The best columbium extraction, 72 pct, was achieved with a sodium fluoride roast at 700° C followed by a 10-pct sulfuric acid leach at 90° C. This method also extracted cobalt and scandium, but not tantalum. Selectivity was poor because iron and manganese were extracted. A processing sequence intended to selectively recover manganese, iron, and columbium was devised and included a sulfuric acid roast and water leaching step followed by an acidic $FeSO_4$ leach and concluded with a NaF-H_2SO_4 leach. Although the tests were successful when tried individually, columbium was not extracted when they were combined sequentially.

TABLE A-4. - Summary of reagents used and composite extraction results from leaching wolframite residues, percent

Technique and reagent	Cb	Co	Fe	Mn	Sc
Roast-leaching:					
H_2SO_4-H_2O.....	0	91	2	95	81
K_2CO_3-HCl.....	0	ND	85	20	0
KOH-HCl.....	13	ND	72	48	0
NaF-H_2SO_4.....	72	78	20	53	76
Leaching:					
$FeSO_4$.....	0	2	67	51	0
$FeSO_4$+H_2SO_4....	0	ND	94	96	ND
30 pct H_2SO_4...	ND	30	86	92	0
60 pct H_2SO_4...	47	84	93	95	0
NaF+H_2SO_4.....	57	49	75	53	48

ND Not determined.